

VERIFICATION OF TRANSLATION

I, Kohei DAIKOUJI
of a citizen of Japan residing at: 2-A, 7-2, Minami-Kugahara
1-chome, Ota City, Tokyo, Japan
certify that I am familiar with the English and Japanese
languages, and to the best of my knowledge and belief the
following is a true translation of the Japanese Patent
Application No. 2002-262314.

This 4th day of March, 2008

Kohei Daikouji

Kohei DAIKOUJI

[Document Name] PATENT APPLICATION
[Identification No.] 34103705
[Submitting Date.] September 9, 2002
[To] Commissioner of Japanese Patent Office
5 [International Patent Classification] G03F 7/038
[Inventor]
[Domicile or Residence] C/O NEC Corporation., 7-1, Shiba 5-
chome, Minato-ku, Tokyo, JAPAN
[Name] Yukinori OCHIAI
10 [Domicile or Residence] C/O NEC Corporation., 7-1, Shiba 5-
chome, Minato-ku, Tokyo, JAPAN
[Name] Masahiko ISHIDA
v[Domicile or Residence] C/O NEC Corporation., 7-1, Shiba 5-
chome, Minato-ku, Tokyo, JAPAN
15 [Name] Junichi FUJITA
[Domicile or Residence] C/O NEC Corporation., 7-1, Shiba 5-
chome, Minato-ku, Tokyo, JAPAN
[Name] Takashi OGURA
[Domicile or Residence] C/O TOKUYAMA Corporation., 1-1,
20 Mikage-cho, Tokuyama-shi, Yamaguchi, JAPAN
[Name] Junji MOMODA
[Domicile or Residence] C/O TOKUYAMA Corporation., 1-1,
Mikage-cho, Tokuyama-shi, Yamaguchi, JAPAN
[Name] Eiji OHSHIMA
25 [Applicant]
[ID number] 000004237
[Name] NEC Corporation
[Applicant]
[ID number] 000003182
30 [Name] TOKUYAMA Corporation
[Attorney]
[ID number] 100071272
[Patent Attorney]
[Name or Title] Yosuke GOTO
35 [Appointed Attorney]

[ID number] 100077838
[Patent Attorney]
[Name or Title] Noriyasu IKEDA

5 [Indication of Charge]

[Deposit Payment Register Number] 012416

[Amount of Fee] 21000yen

[Items of the Filing Articles]

[Article Name] Specification one copy

10 [Article Name] Drawings one copy

[Article Name] Abstract one copy

[General Power of Attorney] 0018587

[Proof] Necessary

15

20

25

30

35

[Document Name] Specification

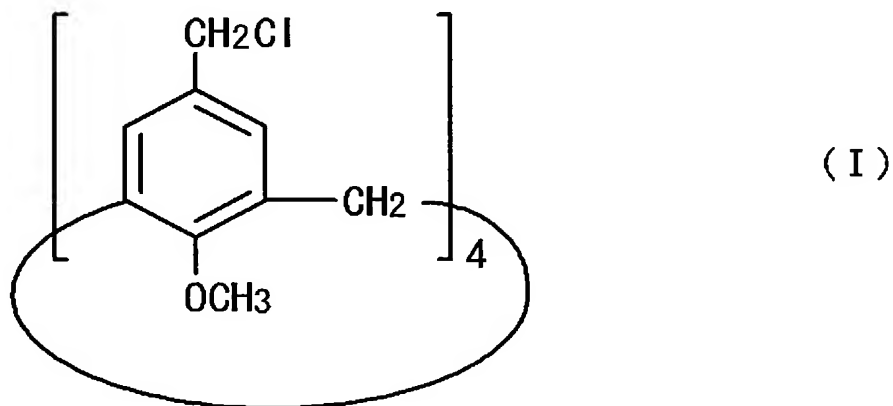
[Title of the invention] RADIATION RESIST

[Scope of Patent to be Claimed]

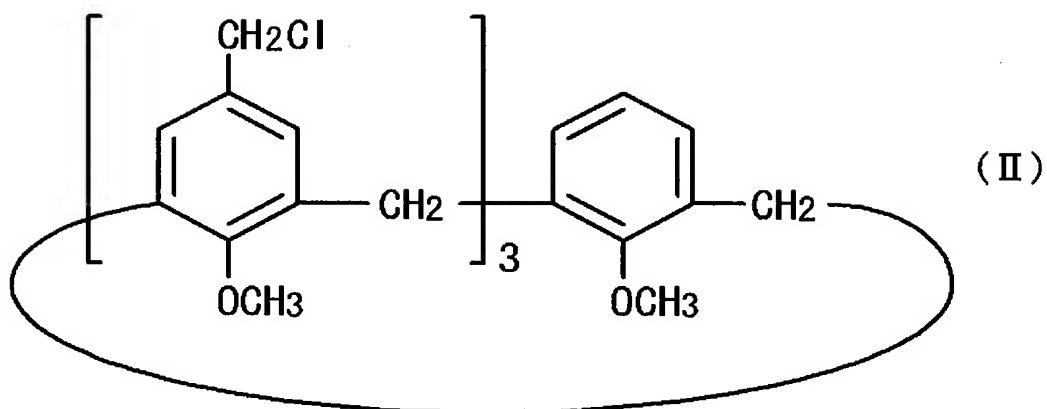
[Claim 1]

5 A calixarene composition comprising at least one of
5,11,17,23 - tetrachloromethyl - 25,26,27,28 -
tetramethoxycalix [4] arene (CMC4AOMe) represented by the
structural formula (I) of the following chemical formula 1 and
5,11,17 - trichloromethyl - 25,26,27,28 - tetramethoxycalix
10 [4] arene (CMC3AOMe) represented by the structural formula
(II) of the following chemical formula 2 as a main effective
ingredient.

[Chemical Formula 1]



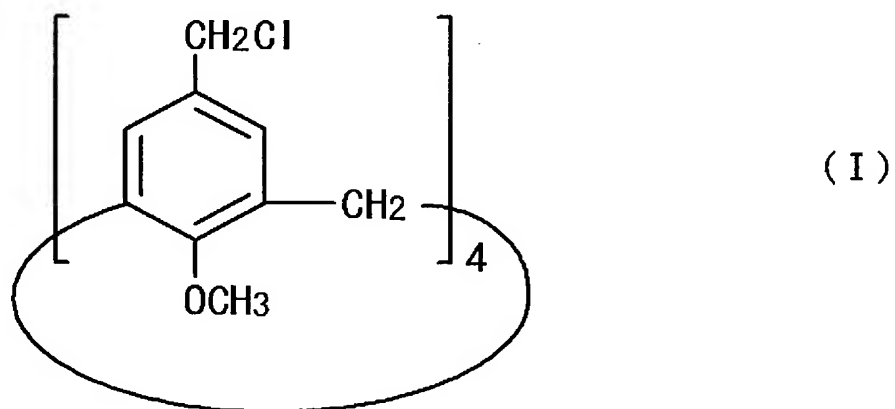
15 [Chemical Formula 2]



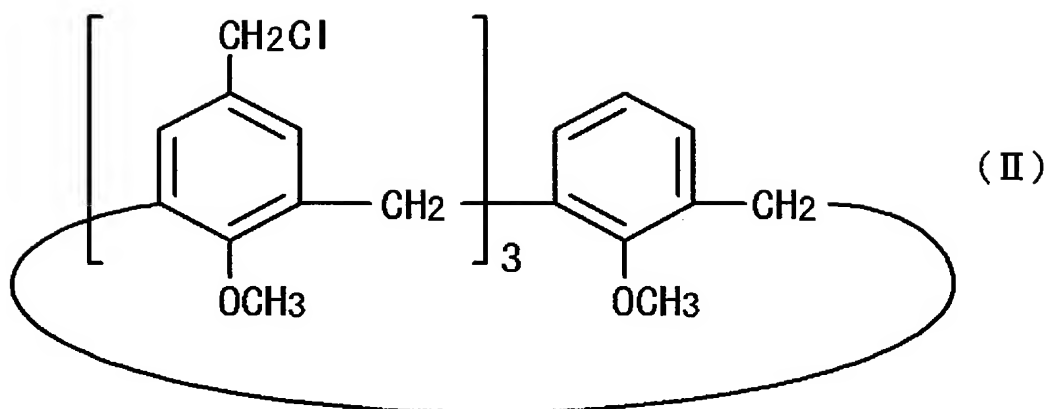
[Claim 2]

A radiation resist comprising at least one of
 5,11,17,23 - tetrachloromethyl - 25,26,27,28 -
 5 tetramethoxycalix [4] arene (CMC4AOMe) represented by the
 structural formula (I) of the following chemical formula 3 and
 5,11,17 - trichloromethyl - 25,26,27,28 - tetramethoxycalix
 [4] arene (CMC3AOMe) represented by the structural formula
 (II) of the following chemical formula 4 as a main effective
 10 ingredient.

[Chemical Formula 3]



[Chemical Formula 4]

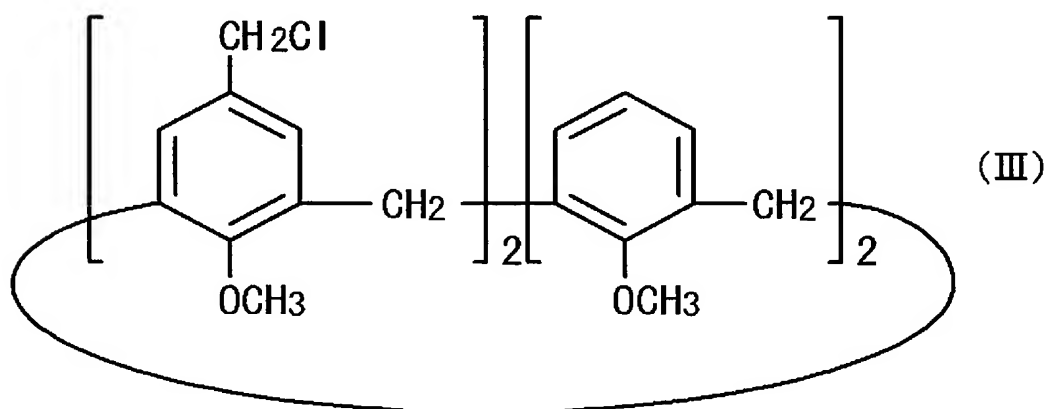


[Claim 3]

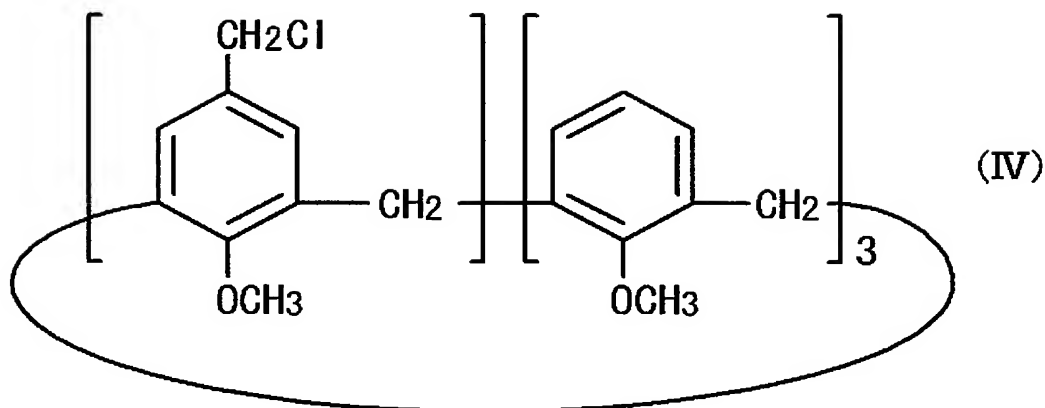
The radiation resist according to claim 2, further comprising at least one of 5,11 - dichloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC2AOMe) represented by the structural formula (III) of the following chemical formula 5 and 5 - monochloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC1AOMe) represented by the structural formula (IV) of the following chemical formula 6 as a main effective

10 ingredient.

[Chemical Formula 5]



[Chemical Formula 6]



[Claim 4]

The radiation resist according to claim 2 or 3,
further comprising at least one of oligomer and polymer
5 macromolecule as a main effective ingredient.

[Claim 5]

The radiation resist according to any one of claims 2
to 4, wherein said radiation is one of or more than two of
electronic beam, X-ray, ion beam and atomic beam.

10 [Claim 6]

A method for forming a radiation resist comprising:
dissolving said resist according to any one of claims 2 to 5
in a safe solvent, coating said resist on a substrate,
exposing said resist, and developing said resist by a
15 developer including a safe solvent.

[Claim 7]

The method for forming the radiation resist according
to claims 6, wherein said safe solvent is at least one solvent
selected from the group consisting of ethyl lactate (EL),
20 propylene glycol monomethyl ether (PGME), propylene glycol
monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl
acetate and 2-heptanone, and

said developer is at least one of said safe solvent
and tetramethyl ammonium hydroxide.

25 [Claim 8]

A method for hyperfine processing comprising the steps of dissolving said radiation resist according to any one of claims 2 to 5 in a safe solvent, coating work with said radiation resist, exposing the radiation resist, developing
5 said radiation resist to form a hyperfine resist pattern, and performing a hyperfine processing with said resist pattern as a mask.

[Claim 9]

The hyperfine processing method according to claim 8,
10 wherein said safe solvent is at least one selected from the group consisting of ethyl lactate (EL), propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate, 2-heptanone, and

15 said developer is at least one of said safe solvent and tetramethyl ammonium hydroxide.

[Detailed Description of the Invention]

[Technical Field to which the Invention belongs]

[0001]

20 The present invention relates to a resist used for pattern formation and etching to form a semiconductor device, a semiconductor integrated circuit or a hyperfine structure. The present invention particularly relates to a resist composed of calixarene derivative for radioactive ray
25 irradiation exposure.

[Conventional Technique]

[0002]

A hyperfine pattern forming technique has been rapidly developed as a forming technique for a semiconductor device
30 or semiconductor integrated circuit. With finer hyperfine structure of the pattern, the higher performance of the individual semiconductor device, namely, the higher speed and the smaller electric power consumption have been attained. Moreover, the improvement of the integration degree of the
35 device leads to the attainment of the semiconductor

integrated circuit having a higher function. Presently, the semiconductor integrated circuits whose circuit dimension (width) is about 130nm are mass-produced.

[0003]

5 In devices used in semiconductor integrated circuits, silicon is used for the substrate. The hyperfine structure limit of the dimension under which the device is operated is said to be about 5nm. Conventionally, optical exposure has been used to form the semiconductor device or integrated
10 circuit. Presently, the optical exposure that uses a krypton fluoride laser having a wavelength of 256nm is used. In order to cope with the hyperfine structure of the finer pattern, the usage of the light having a shorter wavelength is required. As the light expected to be used for the optical
15 exposure of a next generation, argon fluoride laser having a wavelength of 195nm is exemplified. Moreover, as the light expected to be used for the optical exposure of a further next generation, a fluoride laser having a wavelength of 154nm will be implemented. For further future, an extreme
20 ultraviolet exposure having a wavelength of 11 to 13.5 nm, an X-ray exposure having a wavelength of about 1nm and the like are being researched.

[0004]

 On the other hand, since the development of the device
25 itself needs to be started prior to the mass production, an electronic beam exposure technique having versatility is used, although its throughput is low. As the electronic beam exposure technique, a method that has a relatively high throughput and uses a mask is put to practical use and its
30 resolution is about 50nm. On the other hand, the electronic beam exposure that uses a thinly-throttled electronic beam is the exposure technique that jointly attains the practicability and ultra high resolution that enable the formation of any pattern, and the resolution of 50nm or finer
35 is easily realized, and this is used for the research of a

quantum size effect and the trial production of an ultra
hyperfine transistor. The diameter of the electronic beam is
about 1nm in a case of a thin type. However, the minimum
pattern is determined by the resolution of the resist. In the
5 resist that uses an organic molecule having a high
practicability, it is about 10nm in a positive type of PMMA.
[0005]

As negative type and positive type resist compositions,
material employing a poly-ethylene group as a basic skeleton
10 is proposed (see, for example, the patent document 1 and 2).
[0006]

On the other hand, a calixarene resist is proposed as a
negative type resist having the resolution of about 10nm (see,
for example, the patent document 3, 4 and 5).
15 [0007]

In the patent document 3, 4 and 5, it is indicated that
the calixarene resist can be solved in solvent by acetylation.
Also, it is indicated that sensibility of the calixarene
resist to radioactive ray becomes high by chlorination (see,
20 for example, the patent document 6). Through this calixarene
resist, the negative type resist is used to easily carry out
the pattern formation at a 10nm level.
[0008]

A synthesizing method of resist material CMC4AOMe or
25 CMC3AOMe is indicated in, for example, the non-patent document
1.
[0009]

[Patent Document 1]

Japanese Laid Open Patent Application JP-P2001-281864A
30 [0010]

[Patent Document 2]

Japanese Laid Open Patent Application JP-P2002-49153A
[0011]

[Patent Document 3]

35 Japanese Laid Open Patent Application JP-A-Heisei, 6-

53819

[0012]

[Patent Document 4]

Japanese Laid Open Patent Application JP-A-Heisei, 7-

5 23340

[0013]

[Patent Document 5]

Japanese Laid Open Patent Application JP-P2000-330281A

[0014]

10 [Patent Document 6]

Japanese Patent No.2792508

[0015]

[Non-Patent Document 1]

[Tetra-Hedron] written by Nagasaki et al., Vol.48,

15 Page 797-804, 1992

[Problems the Invention Tries to Solve]

[0016]

As mentioned above, the calixarene acts as the negative type resist, and it is useful as an ultra high resolution resist by which the resolution of about 10nm is attained. However, the solvent having capability of dissolving this resist material is the organic solvent including chlorine, such as dichlorobenzene, monochlorobenzene and the like, and the organic solvent such as xylene and the like is used for the development. The usage of these solvents containing chlorine have a tendency to be inhibited as ozone depleting substance and have a tendency to be inhibited because it is not preferred from the viewpoint of a worker's environment.

30 [0017]

A large amount of solvent and developer are used in a pattern forming process, and they are volatile. Thus, the perfect recovery thereof is difficult, which does not allow the usage in the mass production site of the semiconductor integrated circuit or the like.

[0018]

In this way, the conventional calixarene cannot be used in mass production factories that consume a large quantity of solvent and development solution. Although
5 calixarene can be used for laboratorial purposes, the usage in the production of semiconductor devices is difficult. Moreover, in recent years, the expectation for nano-technologies is increased, and the request to the ultra hyperfine pattern of 10nm or less is increased. Thus, the
10 insufficiency of the resolution of the conventional calixarene is indicated.

[0019]

So, a technical object of the present invention is to provide resist material that has a resolution higher than
15 conventional calixarene, and has less problem with work environments, and can be dissolved in a safe solvent, and can be developed by using a development solution containing the solvent, and an exposing method and a hyperfine structure processing method of using it.

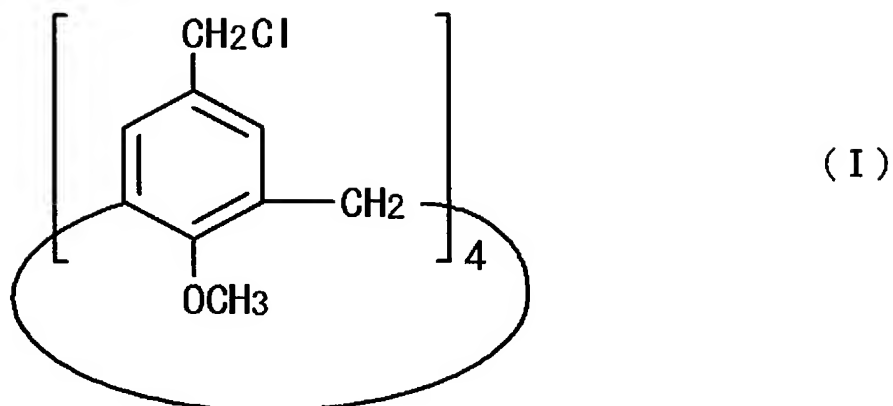
20 [Means for Solving the Problems]

[0020]

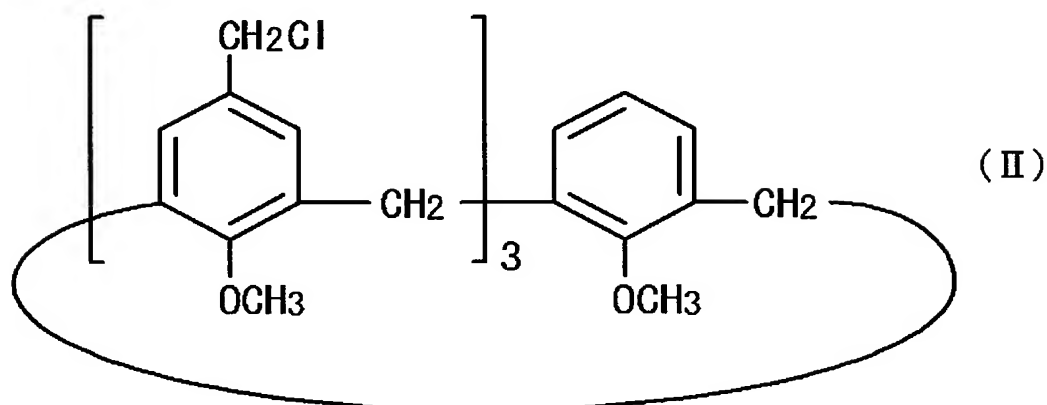
In the present invention, in order to solve the above mentioned problems, many calixarene derivatives are synthesized to test. Consequently, it is found that a resist
25 including at least one of: 5,11,17,23 - tetrachloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC4AOMe) represented by the structural formula (I) of the following chemical formula 5 and 5,11,17 - trichloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC3AOMe)
30 composite represented by the structural formula (II) of the following chemical formula 6 has potential to resolve the problem.

[0021]

[Chemical Formula 7]



[Chemical Formula 8]



Namely, according to the present invention, calixarene
 5 composition including at least one of: the 5,11,17,23 -
 tetrachloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene
 (CMC4AOMe) represented by the structural formula (I) of the
 foregoing chemical formula 7 and 5,11,17 - trichloromethyl -
 25,26,27,28 - tetramethoxycalix [4] arene (CMC3AOMe)
 10 represented by the structural formula (II) of the foregoing
 chemical formula 8 is provided.

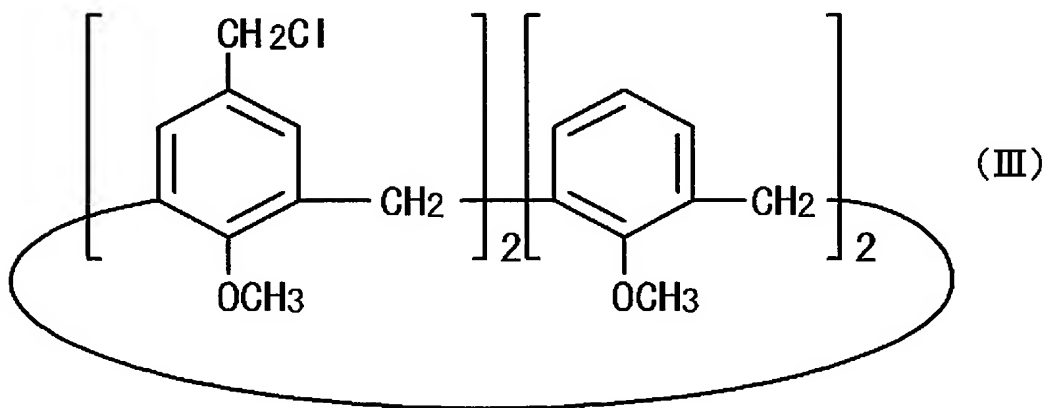
[0022]

Also, according to the present invention, a radiation
 resist including at least one of: 5,11,17,23 -
 15 tetrachloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene

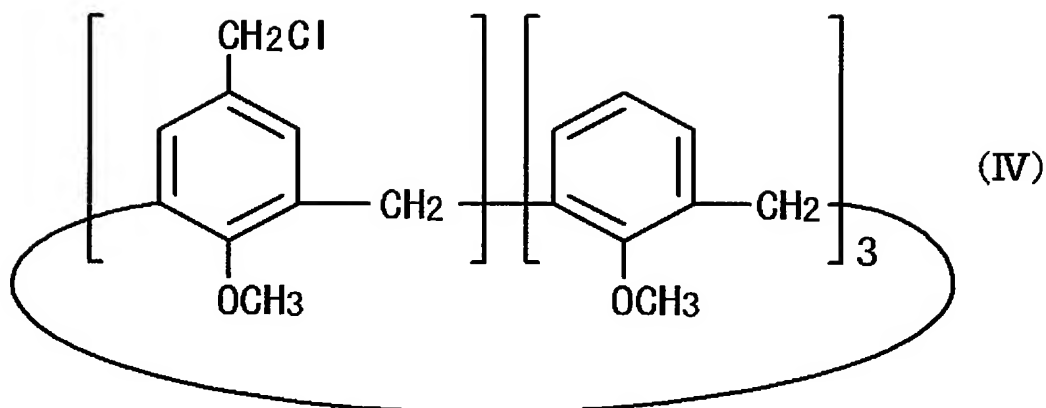
(CMC4AOMe) represented by the structural formula (I) of the foregoing chemical formula 7 and 5,11,17 - trichloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC3AOMe) represented by the structural formula (II) of the foregoing
5 chemical formula 8 as a main active ingredient is provided.
[0023]

Also, according to the present invention, in addition to the above-mentioned radiation resist, a radiation resist further including at least one of: 5,11 - dichloromethyl -
10 25,26,27,28 - tetramethoxycalix [4] arene (CMC2AOMe) represented by the structural formula (III) of the following chemical formula 9 and 5 - monochloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC1AOMe) represented by the structural formula (IV) of the following chemical formula 10
15 as a main active ingredient is provided.
[0024]

[Chemical Formula 9]



[Chemical Formula 10]



Also, according to the present invention, in addition to any of the above mentioned radiation resists, resists further including at least one of oligomer and high molecule as a main active ingredient are provided.

5 [0025]

Also, according to the present invention, in any one of the above-mentioned resists, a radiation resist that is characterized that the radiation is electronic beam, X-ray, ion beam, atom beam or a hybrid beam thereof is provided.

10 [0026]

Also, according to the present invention, a method for forming a radiation resist including the steps of dissolving any of the above mentioned radiation resist by using a solvent excellent in the work environment property as the solvent and coating a substrate by the solution, exposing the radiation resist, and developing the resist by using developer including a solvent excellent in the work environment property.

15 [0027]

Also, according to the present invention, in the method for forming a radiation resist according to claims 6, the safe solvent is at least one solvent selected from the group consisting of ethyl lactate (EL), propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether

20 [0027]

25

acetate (PGMEA), ethyl propionate, n-butyl acetate and 2-heptanone, and the developer is at least one of the safe solvent and tetramethyl ammonium hydroxide.

[0028]

5 Also, according to the present invention, a method for hyperfine processing including the steps of dissolving any one of the above mentioned radiation resist in a safe solvent, coating work with the radiation resist, exposing the radiation resist, developing the radiation resist to form a hyperfine
10 resist pattern, and performing a hyperfine processing with the resist pattern as a mask.

[0029]

 Also, in the method according to the present invention, the safe solvent includes at least one of ethyl lactate (EL),
15 propylene glycol monomethyl ether (PGME), propylene glycol mono-methyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate and 2-heptanone. The developer is, at least one of the above mentioned safe solvent and tetramethyl ammonium hydroxide.

20 [Effect of the invention]

[0030]

 The calixarene represented by the structural formula (I) of the foregoing chemical formula 5 used as the resist of the present invention has 4 benzene rings in the molecule. On
25 the contrary, 5,11,17,23,29,35 - hexachloromethyl - 37,38,39,40,41,42 - hexamethoxy calix [6] arene (CMC6AOMe) that is disclosed in the patent document 6 represented by the structural formula (V) of the following chemical formula 11 has six benzene rings in the molecule and it is different
30 from the present invention.

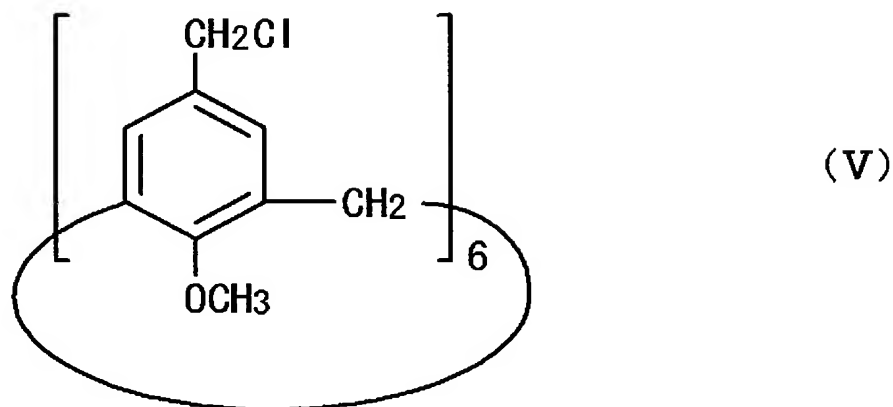
[0031]

 Also, in the case of CMC3AOMe that is used as the resist of the present invention and represented by the structural formula (II) of the above mentioned chemical
35 formula 8, chloromethyl group is coupled to three benzene

rings among four benzene rings, the methoxy group is coupled to the four benzene rings, and the structure is different from CMC6AOMe.

[0032]

5 [Chemical Formula 11]



The calixarene compound used as the resist of the present invention is different in the action in many respects and useful in practical uses, as compared with CMC6AOMe.

10 [0033]

At first, in the compound of the present invention, as compared with the conventional hexachloromethyl hexamethoxy calix [6] arene, the molecular weight is small. Thus, this has the higher resolution and the formation of ultra
15 hyperfine patterns is possible. This is the useful material in nano-technologies in general, such as the biochip and the like, as well as trial productions and manufacture of semiconductor devices. By using the material of the present invention as a resist and forming a pattern and then carrying
20 out a etching process with this resist pattern as the mask, it is possible to process the ground material of the resist and perform the hyperfine processing on the ground material.

[0034]

Moreover, the compound or composition of the present
25 invention can be dissolved in the solvent having less effect to worsen a working environment [so-called safe solvent].

Concretely, they can be dissolved in the solvents which are approved as safe solvents and whose usage is allowed in the semiconductor mass production factory, such as ethyl lactate (EL), propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate, 2-heptanone and the like. These solvents also dissolve many kinds of resist material typically put on markets. Then, the solution of resist using these solvents enables a uniformly thin film to be formed through spin coating on the semiconductor substrate such as silicon and the like. Then, a hyperfine pattern can be formed by exposing and developing the formed film through the electronic beam and the like. As a developer that can be used at this developing process, as well as xylene used as the development solution of CMC6AOMe, safe solvents such as ethyl lactate (EL), propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate and 2-heptanone can be used. Moreover, it can be developed in tetramethyl ammonium hydroxide (TMAH) that is a typical developer used in semiconductor mass production sites.

[0035]

Moreover, in a case of the resist of the present invention includes a composition which containing the mixture of CMC4OMe and CMC3OMe as main ingredients, the dissolubility of the resist to the solvent is improved, thereby the edge roughness property is improved and a sharp pattern can be obtained. The composition ratio between CMC4AOMe and CMC3AOMe is in the range between 99.5:0.5 and 0.5:99.5, preferably between 99:1 and 1:99, and further preferably in a range between 95:5 and 5:95. In the resist, other than the above composition, different types of calixarene and polymers may be included as a component. In such a case also, the dissolubility is improved, and the edge roughness property is improved.

[0036]

The composition including CMC4AOMe or CMC3AOMe and CMC3AOMe of the present invention has the useful property that it can be dissolved in the safe solvent and can be developed by in the safe solvent or tetramethyl ammonium hydroxide. Consequently, this is practical resist material because the problem on the working environment is suppressed and there is no problem even in mass production sites consuming resists such as silicon devices and the like.

10 [Embodiments of the Invention]

[0037]

Embodiments of the present invention will be described below with reference to the accompanying drawings.

[0038]

15 Fig. 1 is a flow chart showing the synthesizing method of a resist and the forming method of a hyperfine pattern according to an embodiment of the present invention. As shown in Fig. 1, CMC4AOMe or CMC3OMe that is the resist material is synthesized by using the method disclosed in the above mentioned non-patent document 1.

20 [0039]

At first, 25,26,27,28 - tetramethoxy calix [4] arene that is raw material is dissolved in dioxane of 50-time amount. Para formaldehyde of 40 mol times, acetic acid of 5 time amount and 85% phosphoric acid of 10 time amount are added, and heated and agitated for 8 hours at 100 celsius degree. After the reaction, the reaction solution is poured into water with ice, and deposited white solid is filtered and extracted.

30 [0040]

As the synthesizing process, the foregoing solid is dissolved in chloroform, and water is added, and they are washed until a water phase becomes neutral. After a chloroform phase is dried with magnesium sulfate, it is concentrated to obtain a composition (Step S1). This

composition is refined with silica gel column chromatography (developing solvent/ethyl acetate : hexane = 1:7) (Step S2).

[0041]

5 The derivative of the calixarene obtained by the purification is mixed at a proper mixture ratio as necessary and made into the composition. Also, oligomer and polymer are added and mixed.

[0042]

10 Next, the material or composition obtained by the synthesis is dissolved in the solvent (Step S3).

[0043]

Here, as the solvent, non-safe solvent such as monochloro benzene or dichloro benzene can be used. However, since the property being dissoluble in safe solvents is a
15 feature of the present material, it is preferable to use safe solvent such as ethyl lactate (EL), propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate, 2-heptanone and the like for dissolution. The use of the stylus
20 and the like is effective for agitating for dissolving sufficiently. The solvent which can be used is not limited to the solvents explained here.

[0044]

Next, as a coating step, the prepared solution is
25 coated on a work such as a silicon substrate or the like by the spin coating method. The substrate may be the silicon substrate as indicated in Step S4a, a substrate with a film as indicated in Step S4b or a substrate with a hard mask as indicated in Step S4c. The film thickness to be coated is
30 adjusted by controlling the rotation number. After the spin coating, there may be a case of carrying out a heating step referred to as the pre-bake for vaporizing the solvent. The heating is carried out by, for example, an oven or a hot plate in nitrogen atmosphere at a temperature between about
35 80°C and 170°C. The period is between about 1 minute and

several hours. It is preferable to optimize the process condition according to the desired processing. In a typical coating condition, the rotation number of 3000rpm between 30 seconds and 1 minute is implemented to obtain a film
5 thickness of about 30 nm after the pre-baking. This film thickness is desired to be properly adjusted, depending on the etching depth and the etching ratio between the processing target and the resist. As the substrate to be coated, a silicon substrate itself, and the silicon substrate
10 with silicon oxide film, poly-silicon film or aluminum film can be employed. Other than these, the work film can be selected according to requirements. Also, if the processing depth of non-processed film is deep or when the etching speed is not high, an intermediate film referred to as the hard
15 mask is preliminarily formed on the work film. Once the pattern formed with the resist is transcribed into this intermediate film, the intermediate film having a high etching resistance is used as the mask, and the work under it can be efficiently processed by etching. As the hard mask,
20 the film such as silicon oxide film, silicon nitride film and the like are generally used.

[0045]

Next, after the coating, the resist film is exposed with the radioactive ray (Step S5). When the hyperfine
25 pattern is formed, the electronic beam is used to expose in many cases. The beam diameter of the electronic beam can be thinned to about several nm, and it is suitable for the formation of super hyperfine patterns. Also, other than the electronic beam, the exposing can be carried out by using the
30 ultraviolet ray, the X-ray, the extreme ultraviolet ray (EUV), the ion beam, the atomic beam and the like, which are used in the typical optical exposure.

[0046]

Next, the exposed resist film is developed (Step S6).
35 For the development, ethyl lactate (EL), propylene glycol

monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate, 2-heptanone and the like, which are used as the solvent of the resist material, and tetramethyl ammonium hydroxide, xylene
5 and the like can be used. Basically, a solvent in which the dissolution speed of the exposure portion and non-exposure portion are different can be used as the developer. In the development, the exposed resist or sample is dipped in or brought into contact with the developer for about 30 seconds
10 to several minutes. This resist becomes hard to dissolve in the developer as the radiated radioactive ray amount is increased to form the pattern. In this way, this resist acts as the negative type resist.

[0047]

15 Fig. 2 is a view showing an example of the exposure property of the resist according to the embodiment of the present invention. The resist is the composition of 5,11,17,23 - tetrachloromethyl - 25,26,27,28 - tetramethoxycalix [4] arene (CMC4AOMe) / 5,11,17-
20 trichloromethyl - 25,26,27,28 - tetramethoxy calix [4] arene (CMC3AOMe) = 7/3. The composition is dissolved in ethyl lactate, and exposed through the Gaussian electronic beam of 50 kV accelerated, and developed with ethyl lactate or xylene. The lateral axis indicates the irradiated electronic beam
25 amount, and the longitudinal axis indicates the film thickness after the development.

[0048]

Fig. 2 shows the property of the mixture in which 5,11,17,23 - tetrachloromethyl - 25,26,27,28 -
30 tetramethoxycalix [4] arene (CMC4AOMe) in the structural formula (I) and the 5,11,17-trichloromethyl - 25,26,27,28 - tetramethoxy calix [4] arene (CMC3AOMe) are mixed at the rate of 7:3 in the molecular number ratio. The irradiated electronic beam is the Gaussian beam type electronic beam of
35 an acceleration voltage 50kV. Ethyl lactate is used as the

solvent, and ethyl lactate and xylene are used as the development. The property of CMC6AOMe is also indicated for the comparison. As the amount of the electronic beam irradiation increases, the more resist film remains without
5 dissolving in the development solution after the development. In both of the ethyl lactate and the xylene, when the film is irradiated at the irradiation amount of about $1\text{mC}/\text{cm}^2$, about half of the film thickness remains, and when the film is irradiated at the irradiation amount of about $2\text{mC}/\text{cm}^2$, the
10 film thickness substantially same to that of the time of the coating remains. The exposure amount at which the film thickness at the time of the coating remains is typically referred to as a resist sensibility. The ethyl lactate development is slightly higher in sensibility than the xylene
15 development. It is recognized that a comparison example CMC6AOMe is further higher in the sensibility. The reason is considered such that because of the difference in the molecular weight, CMC4AOMe or the mixture of CMC4AOMe and CMC3AOMe requires more electronic beam irradiation in order
20 to obtain the same polymerization degree of C6AOMe.

[0049]

The sensibility of the resist shown in Fig. 2 is lower as compared with the sensibility of resists typically put on markets. However, with the higher resolution, the sensibility
25 tends to be lower. The sensibility of MC6AOAc that is not chlorinated is bad such as $10\text{mC}/\text{cm}^2$. The present resist has a relatively high sensibility though having a high resolution.

[0050]

Fig. 3 and Fig. 4 are electronic microscope images
30 showing an example of the developed resist pattern according to an embodiment of the present invention. In Fig. 3, development is carried out by using xylene, and in Fig. 4, development is carried out by using ethyl lactate, and in either figure, silicon is used as the substrate. In both
35 cases, the line pattern was formed by the exposition using

the Gaussian beam of 50 kV to draw one line. In any of the examples, the line width is about 8nm, which shows very high resolution. The resist patterns shown in Fig. 3 and Fig. 4 are formed by using the resist containing the mixture of
5 5,11,17,23 - tetrachloromethyl - 25,26,27,28 -
tetramethoxycalix [4] arene (CMC4AOMe) in the structural
formula (I) and 5,11,17-trichloromethyl - 25,26,27,28 -
tetramethoxy calix [4] arene (CMC3AOMe) in the chemical
formula 2 in which the mixed ratio of 7 : 3 in the molecular
10 number ratio. The sensibility is high and the high resolution
pattern in which the line width is 8nm is obtained.

[0051]

Also, as the resist composition, the composition in
which any one or both of 5 - monochloromethyl - 25,26,27,28 -
15 tetramethoxycalix [4] arene indicated in the structural
formula (IV) of the chemical formula 4 or chemical formula 8
and 5,11 - dichloromethyl - 25,26,27,28 - tetramethoxycalix
[4] arene of the chemical formula 3 are mixed with the
compound of the foregoing structural formula (I) is allowable
20 to use. Moreover, oligomer of a proper molecular weight and
organic high molecular compound other than calixarene may be
mixed. The resist made of these composition can be dissolved
in safe solvents and has the sensibility to the radioactive
ray, and can be developed with safe solvents, and enables the
25 formation of the hyperfine pattern and can be used for the
formation of the hyperfine shape.

[0052]

As explained above, this resist is used to form
hyperfine resist patterns. After that, as necessary, with
30 this resist pattern as the mask, the under layer is etched.
As the etching, the dry etching that uses the plasma or the
ion, and the wet etching that uses the solution can be
applied. In order to form the hyperfine shape at a high
precision, the dry etching is generally used. For example,
35 the sputtering that uses the argon ion or the milling is used

to etch the underlying work. In order to etch more efficiently, the reactive ion etching is employed in which the applied ion, namely, the gaseous species or the mixture ratio of gases is adjusted depending on the material of the work. For example, fluorine-based gas or bromine-based gas is used to etch the silicon oxide film. Chlorine-based gas is used to etch the compound such as gallium arsenide and the like. Concretely, the gas such as CF_4 , CHF_3 , CClF_2 , BCl_3 , CBrF_3 , SF_6 and the like, or the gas in which oxygen or argon gas is mixed with the foregoing gas is used. There are many combinations of gaseous species and mixtures thereof. And if the etching speed of the target work is not very faster or slower than the etching speed of the resist mask, the resist pattern is once transcribed into an intermediate film having a high etching resistance, and the under layer is processed with this intermediate film as the mask. In this case, when the resist pattern is transcribed into the intermediate film, the gaseous species in which a certain level of the etching speed can be obtained is used. When the under layer is etched with the intermediate film as the mask, the gaseous species is changed to obtain a certain level of the etching speed ratio between the intermediate film and the ground. Also, there are many kinds of the methods for generating the ion and the plasma, and any of them can be applied.

[Effect of the invention]

[0053]

As being explained above, the radiation resist according to the present invention has high resolution of forming patterns of even below 10 nm. A material useful for nano-technology such as finer hyperfine semiconductor device, researches of quantum effects and the manufacture of biochips.

[0054]

Further, the radiation resist according to the present invention is soluble in solvents which are safe to the human body and loads to environment is less. As a result, it can be

used especially in locales in which a large amount of the resist is used such as a semiconductor production factory.

[Brief Description of the drawings]

[Fig. 1]

5 A flow chart showing the synthesizing method of the resist and the hyperfine pattern forming method according to an embodiment of the present invention.

[Fig. 2]

10 A view showing an example of the exposure property of the resist according to an embodiment of the present invention.

[Fig. 3]

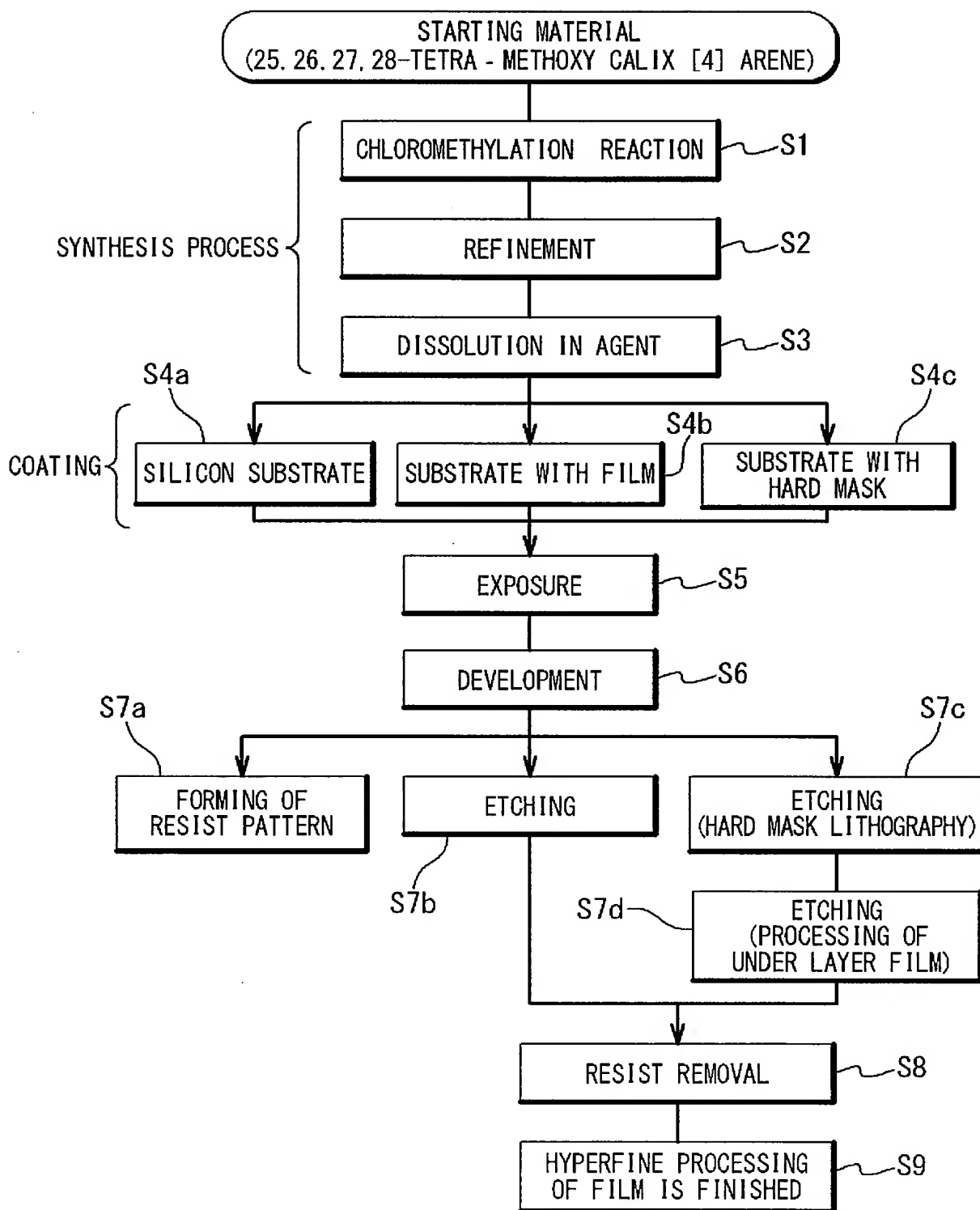
15 An electronic microscope image indicating an example of a line pattern obtained by exposing and developing the resist according to an embodiment of the present invention through the electronic beam, in which silicon is used as the substrate and xylene is used as the developer.

[Fig. 4]

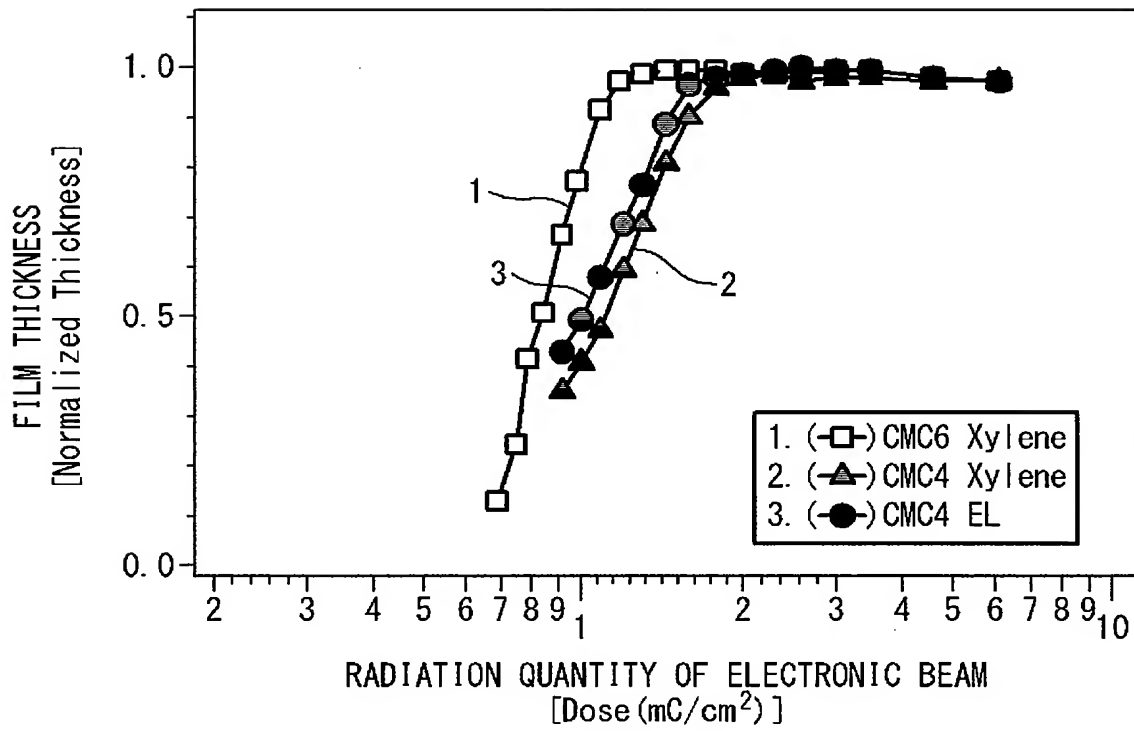
20 An electronic microscope image indicating an example of a line pattern obtained by exposing the resist according to an embodiment of the present invention through the electronic beam and developing it, in which silicon is used as the substrate, and ethyl lactate is used as the developer.

[Document Name] Drawings

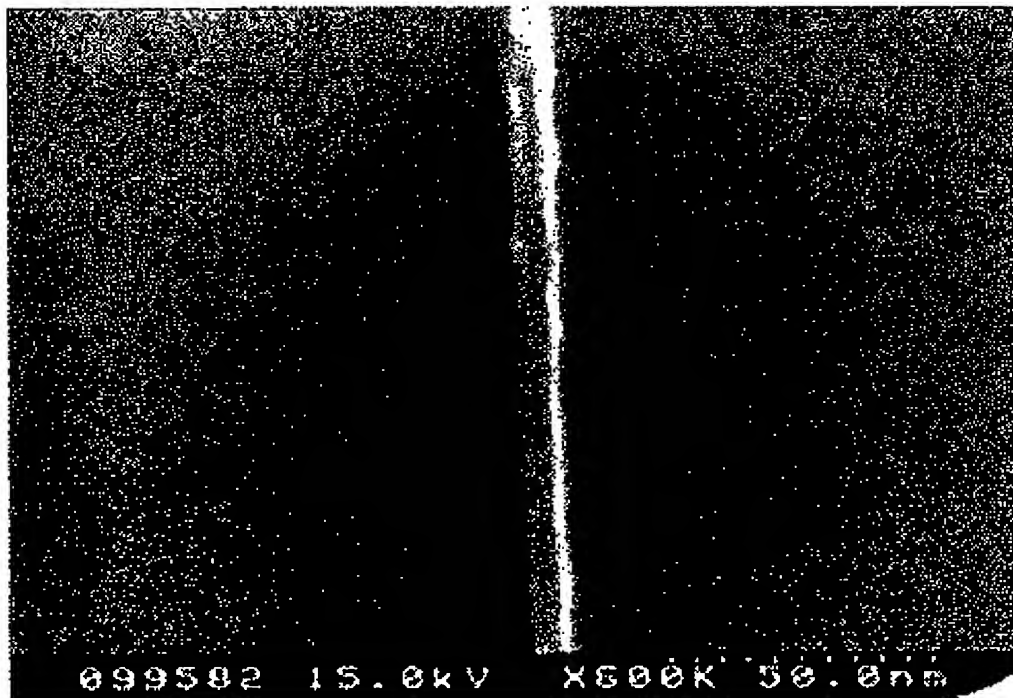
[Fig. 1]



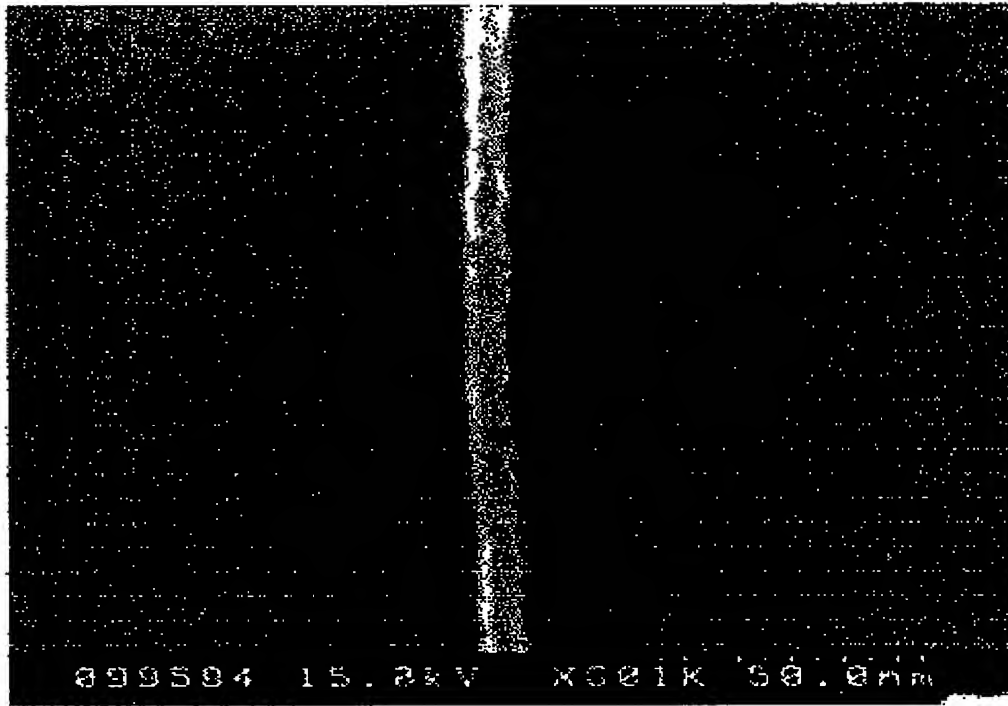
[Fig. 2]



[Fig. 3]



[Fig. 4]



[Document Name] Abstract

[Abstract]

- 5 [Problem to be Solved] To provide photosensitive resist material whose resolution is high, soluble to safe solvents and safe solvent developable, and to provide an exposing method and hyperfine manufacturing method using the resist material.
- 10 [Means for Solving the Problem] A radiation resist includes one or both of tetrachloromethyl - tetramethoxycalix [4] arene and trichloromethyl - tetramethoxycalix [4] arene (CMC3AOMe) as main effective ingredients. The resist material is soluble in a safe solvent, for example, ethyl lactate (EL), propylene
- 15 glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl propionate, n-butyl acetate and 2-heptanone. The development can be performed by one of the safe solvents exemplified above and tetramethyl ammonium hydroxide.
- 20 [Selected Drawing] Fig. 1